



Investigation of cathode electrocatalysts composed of electrospun Pt nanowires and Pt/C for proton exchange membrane fuel cells

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HIGHLIGHTS

- Electrospun Pt-NWs are fabricated by PVP-Pt nanofibers as precursors.
- Electrocatalysts composed of Pt-NWs and Pt/C on ORR activity is investigated.
- Exploring the optimal mixing ratio of Pt-NWs and Pt/C in the cathode of a PEMFC.
- Pt/C mixed with a small amount of Pt-NWs shows better performance than pure Pt/C.
- The optimal Nafion content in the electrode using such a composite catalyst is 30%.

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ABSTRACT

The present work investigates the effect of cathode electrocatalysts composed of Pt nanowires (Pt-NWs) fabricated by electrospinning method and commercial Pt-loaded carbon black (Pt/C) on the oxygen reduction reaction (ORR) in a proton exchange membrane fuel cell. Pt nanowires are prepared by heating electrospun polyvinyl pyrrolidone (PVP)-Pt composite fibers at high temperatures in air atmosphere. Cathode catalyst layers with different mixing ratios of Pt-NWs and Pt/C are tested to explore their activities toward ORR. The results show that the conventional Pt/C mixed with a small amount of Pt-NWs exhibits better catalytic performance than the pure Pt/C catalysts. Under the same Pt loading of 0.5 mg cm^{-2} , the case of composite electrocatalyst of 0.1 mg cm^{-2} Pt-NWs and 0.4 mg cm^{-2} Pt/C presents the best catalytic activities which can be rationalized by enhanced electrochemical surface area and exchange current density in the catalyst layer. The effect of Nafion content is also evaluated and the results show that the optimal content of Nafion ionomer is 30 wt% using such a composite electrocatalyst in cathode catalyst layer.

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1. Introduction

Proton exchange membrane fuel cell (PEMFC) performance depends heavily on the use of platinum (Pt) in membrane electrode assembly (MEA) as electrocatalysts especially in cathode electrode. Since Pt is an essential but very expensive element in MEA, it is still an important issue in the development of PEMFC technology regarding how to improve Pt utilization and reduce the amount of Pt use in MEA. Numerous studies in the literature have devoted to this research field. Detailed reviews could be found in the recent works [1–3]. In general, the electrocatalysts in catalyst layer are prepared by Pt supported on carbon black (Pt/C) like Vulcan XC-72R

which is a widely used support material for Pt particles. However, such a conventional Pt/C structure suffers from low Pt utilization due to the difficulty for the Nafion ionomer to form a triple-phase boundary with Pt particles entering the mesopores on the surface of carbon black [3]. Therefore, enormous effort has focused on how to improve the electrocatalytic properties of Pt by employing different support materials or synthesizing Pt particles in various structures. Recently, electrospinning technique has been used to fabricate new catalysts for PEMFCs with high activity and good durability [4]. The one-dimensional nanostructure of electrocatalysts produced by electrospinning demonstrates efficient use of catalyst by decreasing embedded sites in the interfaces between electrode and electrolyte, and provides facile pathways for the charge transfer between catalytic particles. Thus, the electrospun Pt or Pt-based nanowires have been widely studied to improve liquid fuel oxidation performance such as cyclohexane [5] or methanol

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[6–8] at anode electrode. However, nanowire catalysts possess smaller specific surface areas than nanoparticles which may result in less electrochemical surface area (ESA). This characteristic may restrict the application of Pt nanowires (Pt-NWs) for the cathode electrode in a conventional hydrogen-fueled PEMFC with low Pt loadings [9–11]. Kim et al. [9] first proposed composite electrocatalysts composed of Pt-based nanoparticles and nanowires for the preparation of anode electrodes and investigated the effect on the low temperature fuel cell performance. They found such a hybrid composite of electrocatalysts could enhance the activity of anode electrode toward hydrogen or methanol oxidation significantly. They further considered oxygen reduction reaction (ORR) in cathode catalyst layer by employing the composite catalysts made by highly-dispersed Pt/C into electrospun Pt-NWs [10]. Their results show the ORR activity can be improved greatly than the conventional Pt/C catalysts alone. The effect of Pt-NW loading on ORR activity also has been examined by the method of directly growing Pt-NWs onto gas diffusion layer [11]. Note that in the studies [9,10] the composite catalysts are made up by mixing Pt/C and Pt-NWs with equal Pt mass. The optimal mixing ratio of both Pt/C and Pt-NWs is still unknown, which motivates the present investigation. The other important component in the catalyst layer is the Nafion ionomer which may affect the catalytic activity, ionic resistance, gas permeability and formation of triple-phase boundary significantly. Several studies in the literature [12–19] had considered the influence of Nafion content in catalyst layer on PEMFC performance. Particularly, the recent work done by Du et al. [18] has considered the effect of Nafion loading on the gas diffusion electrode with in-situ grown single crystal Pt nanowire. However, the optimal Nafion content in such a catalyst layer made by composite electrocatalysts of Pt/C and Pt-NWs still has not been evaluated.

In the present study, we examine the effectiveness of composite electrocatalysts composed of electrospun Pt-NWs and conventional Pt/C on ORR performance in a PEMFC. Cathode catalyst layers were prepared with different mixing ratios of Pt-NWs and Pt/C to explore their activities toward ORR and determine the optimal mixing ratio. The techniques of electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were respectively used to characterize various potential losses and variation of electrochemical surface area (ESA). The corresponding optimal Nafion content is also investigated. The results provide a more complete understanding for a cathode catalyst layer using Pt-NW network structure mixed with highly-dispersed Pt/C particles and benefit the development of highly active electrode for PEMFC system.

2. Experimental

2.1. Preparation of Pt nanowires

A polyvinyl pyrrolidone (PVP, Mw = 1,300,000) polymer solution mixed with a Pt precursor was prepared before the electrospinning process. An appropriate amount of PVP powder was dissolved in ethanol first and then mixed with a Pt precursor solution made of hydrogen hexachloroplatinate hydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) and deionized (DI) water. The solution was stirred continuously for 12 h to produce an aqueous solution containing 8 wt% of PVP and 6.5 wt% of Pt. The resultant homogeneous solution of PVP-Pt precursor was transferred to the electrospinning apparatus immediately for the collection of electrospun polymer nanofibers. The distance between the syringe tip and the fiber collecting plate was 15 cm with an applied voltage 18 kV. The flow rate of the electrospinning solution was fixed at 1.0 ml h^{-1} and the whole process was performed at room temperature with humidity under 40%. Next, the as-spun nanofibers were removed from the

collecting plate and calcined in an oven to obtain Pt nanowires. The PVP-Pt polymer fibers were first heated to 260°C with heating rate $0.3^\circ\text{C min}^{-1}$ and held for 1 h. The heating temperature was then raised to 350°C with heating rate $0.75^\circ\text{C min}^{-1}$ and held for 1 h. Finally, the heating temperature was increased to 450°C with heating rate $0.75^\circ\text{C min}^{-1}$ and held for 1 h in an air atmosphere to burn away of the carbonized polymer.

2.2. Preparation of MEA and performance characterization

The obtained Pt nanowires were mixed with commercial Pt/C catalysts (20 wt%, E-TEK) to fabricate the cathode electrode. The solution containing Pt-NWs and Pt/C was prepared first in DI water and 2-propanol and sonicated in an ultrasonic cleaner for 1.5 h. An appropriate amount of Nafion solution was then added and the solution was sonicated again for 1.5 h and agitated by a dispersing instrument for 2 h to ensure sufficient mixing of Pt-NWs and Pt/C. Carbon cloth (LT140EW, E-TEK) with microporous layer (MPL) coating was used as gas diffusion media and washed by acetone first before the coating of catalyst layer. The catalyst slurry was brushed carefully on the MPL surface and then the catalyst-coated carbon cloth was dried in an oven with air circulation at 70°C . This process repeats several times until the assigned Pt loading was reached. The anode electrode was fabricated in the same way with purely commercial Pt/C as electrocatalysts. The amount of Pt loading is fixed at 0.5 mg cm^{-2} and the Nafion content is 25 wt% in all the experiments. Nafion 115 (DuPont) was used as the proton exchange membrane. Prior to fabricate MEA, the membrane should be treated [13] to convert the membrane fully to the H^+ form. Finally, the MEA with reaction area $2 \text{ cm} \times 2 \text{ cm}$ was made by sandwiching the membrane between anode and cathode electrodes and hot pressing at 135°C and 150 kg cm^{-2} for 90 s.

A single cell with the homemade MEA was constructed by applying a uniform torque of 35 kgf cm on the eight bolts that were used to assemble the fuel cell. The cell performance was measured by a Hephas[®] fuel cell test station. Pure hydrogen and air were employed as the reactant gases in anode and cathode, respectively. Both gas streams were fully humidified and the fuel cell temperature was held at 70°C . During the testing procedures, the flow rates of hydrogen and air were initially held at minimum values of 150 sccm and 350 sccm, respectively, and then increased automatically with stoichiometric value of 2 for both hydrogen and air streams. The outlets of gas streams were open to atmosphere so the MEA was operated at atmosphere pressure. A frequency response analyzer (FRA) module added to an Autolab PGSTAT 302N potentiostat was employed to perform the EIS measurements and characterize the individual contribution to cell resistance. The sweeping frequency was between 0.1 Hz and 10 kHz and the obtained spectra were further analyzed by an equivalent circuit. Cyclic voltammetry measurements were also conducted in-situ to investigate the influence of composite electrocatalysts on electrochemical surface area. The cathode as working electrode was purged with nitrogen, while the anode as counter/reference electrode was fed with hydrogen. Accordingly, the atomic hydrogen adsorption charge density could be estimated from the CV scan and determine the ESA of the Pt catalyst. Morphology of Pt-NWs was observed by scanning electron microscope (SEM, JEOL, JSM-5600) and equipped energy dispersive spectroscopy (EDS) was used to examine the element composition on nanowire surface. The morphology of electrode surface was observed by SEM (JEOL, JSM-6700) and atomic composition on the cross-sectional area of catalyst layer was measured by X-ray photoelectron spectroscopy (XPS, JEOL, JPS-9200) to inspect the Pt distribution.

3. Results and discussion

Fig. 1(a) and (b) shows the SEM images of electrospun PVP-Pt nanowires before and after calcination, respectively. The mean fiber diameter is estimated by averaging randomly 20 points on the image. It is found that the mean diameter reduces from 123 ± 25 nm to 85 ± 19 nm before and after calcination treatment. Fig. 1(c) shows the surface of cathode catalyst layer for the typical case of 0.1 mg cm^{-2} Pt-NWs mixed with 0.4 mg cm^{-2} Pt/C. We can observe that Pt-NWs were embedded into Pt/C as those indicated by some arrows. By cutting the gas diffusion electrode in liquid nitrogen, the cross-sectional area of catalyst layer was observed under SEM as shown Fig. 1(d). One can see that the Pt-NWs were well dispersed in the catalyst layer and the nanoparticles of Pt/C wrapped around Pt-NWs and attached to Pt-NWs uniformly. To further identify the uniformity of Pt distribution, XPS analysis was carried out for the cross-sectional area in the catalyst layer. The test conditions are as follows. X-rays for excitation are non-monochromatic Mg K α . Measurement energy resolution for the photoelectron peak was 0.9 eV at pass energy of 10 eV. Each area for XPS analysis is $1 \mu\text{m}$ in diameter. The intensity of a peak in an XPS spectrum was measured by integrating the recorded counts per second minus a computed background over an energy interval delimiting the peak. The weight percentage of Pt was measured for ten random areas in the composite electrocatalysts of Pt/C and Pt-NWs. The XPS result shows that the percentage of Pt was $69.2 \pm 5.4 \text{ wt\%}$ (mean \pm standard deviation). The ANOVA (analysis of variances) analysis supports that there was no difference in Pt amounts in these ten areas. Besides, the standard deviation in Pt amount was less than 10%, suggesting the uniform distribution of Pt in the composite catalyst layer. Since the distribution of Pt was highly uniform, it was inferred that the Pt/C was well dispersed in

Pt-NWs. Similar results also could be observed in the other cases with different mixing ratios of Pt/C and Pt-NWs. In the following discussion, we first pay attention to the optimal mixing ratio of Pt-NWs and Pt/C and then evaluate the optimal Nafion content in cathode catalyst layer using such a composite electrocatalyst.

3.1. Evaluation of optimal mixing ratio of Pt-NWs and Pt/C

Fig. 2 shows the polarization curves at different mixing ratios of Pt-NWs and Pt/C. The total amount of Pt loading and Nafion content in all the cases are fixed at 0.5 mg cm^{-2} and 25 wt%, respectively. We first make the cathode electrode employing pure Pt-NWs as electrocatalysts. However, its performance is worse than that of totally using conventional Pt/C catalysts which is in agreement with the findings of Kim et al. [10]. While if some of the Pt-NWs is replaced by Pt/C, it is found that the cell performance increases gradually and may exhibit better performance than the case of pure Pt/C. One can see that the case of (Pt-NWs, Pt/C) = (0.1, 0.4) in unit of mg cm^{-2} gives the highest peak power density. The present results reveal that the composite electrocatalysts of Pt-NWs and Pt/C indeed may enhance the cell performance and a small amount of Pt-NWs mixed with Pt/C is favorable. In order to explore the characteristics of such a composite electrocatalyst layer, the EIS technique was employed to characterize the variations in charge transfer resistance, ohmic resistance, and gas transfer resistance. A typical test result is illustrated in Fig. 3 at current density 500 mA cm^{-2} with different mixing ratios of Pt-NW and Pt/C. Two distinct arcs can be observed in each spectrum which is a general pattern for a hydrogen/air PEM fuel cell. The high-frequency arc on the left indicates the effective charge transfer resistance for the oxygen reduction reaction in the catalyst layer, and the low-frequency arc on the right mainly represents the transport

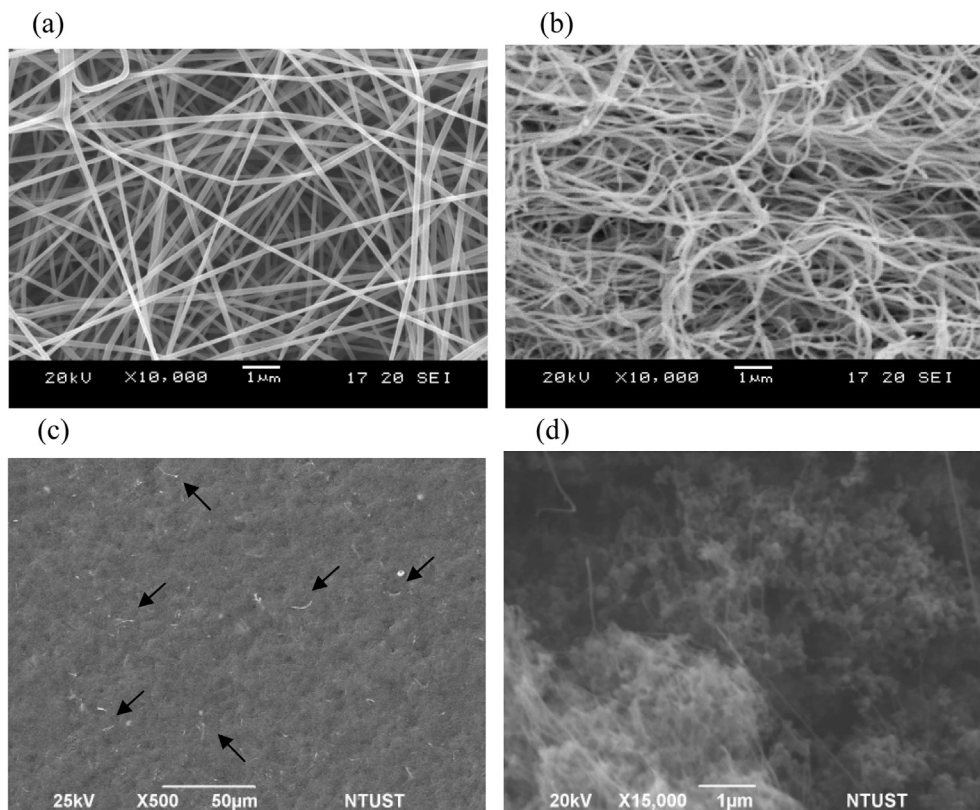


Fig. 1. SEM images of PVP-Pt precursor composite nanowires before (a) and after (b) calcination processes, (c) the electrode surface image of hybrid Pt-NWs and Pt/C, and (d) the corresponding cross-sectional image of catalyst layer.

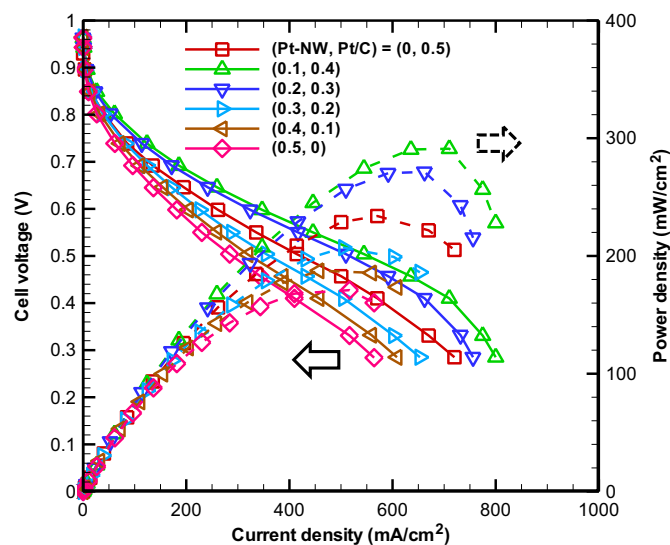


Fig. 2. Polarization and corresponding power density curves at different mixing ratios of Pt-NW and Pt/C in unit of mg cm^{-2} .

resistance of air through the gas diffusion media. The intercept of horizontal real axis with the impedance spectrum at the end of the left arc indicates the ohmic resistance of the fuel cell. A generally proposed equivalent circuit was used to simulate the impedance data and the results are listed in Table 1. Obviously, the influence of cathode catalyst layer composition on ohmic resistance is insignificant since the variation in ohmic resistance in all the cases is almost negligible. The ohmic resistance is primarily dominated by the proton conductivity through the electrolyte membrane which depends heavily on the water content within the membrane. The present results show that the variation in cathode catalyst layer composition does not affect the water content in the electrolyte membrane and produce no effect on the ohmic resistance of the fuel cell. But its influences on charge transfer resistance and gas transfer resistance are relatively significant as shown in Fig. 3 and Table 1. The case of (Pt-NWs, Pt/C) = (0.1, 0.4) mg cm^{-2} obviously gives the lowest charge transfer resistance and gas transfer resistance in all the considered cases. As the amount of Pt-NW increases in the composite catalyst, the diameter of the high frequency arc increases, reflecting the decreasing driving force for ORR and increasing the charge transfer resistance. Similar behaviors also can be observed for the low frequency arc which increases in size consistently with the amount of Pt-NW in the composite catalyst. But the variation in gas transfer resistance is relatively smaller than the charge transfer resistance. This result indicates that a small and appropriate amount of Pt-NW is helpful for the enhancement of

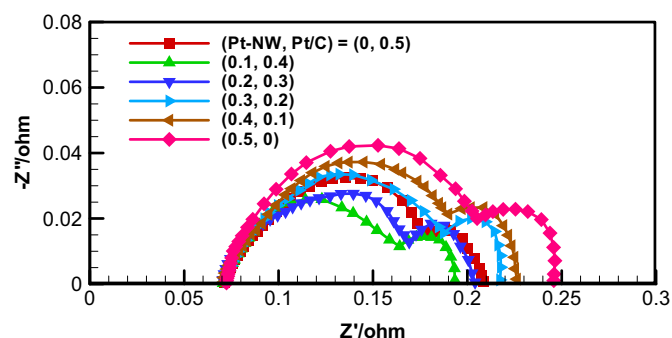


Fig. 3. Impedance spectra measured at current density 500 mA cm^{-2} for different mixing ratios of Pt-NW and Pt/C in unit of mg cm^{-2} .

Table 1

Characteristics of the MEAs with cathode electrodes prepared by different mixing ratios of Pt-NW and Pt/C.

(Pt-NW, Pt/C) (mg cm^{-2})	Ohmic resistance ($\text{m}\Omega \text{ cm}^{-2}$)	Charge transfer resistance ($\text{m}\Omega \text{ cm}^{-2}$)	Gas transfer resistance ($\text{m}\Omega \text{ cm}^{-2}$)	ESA ($\text{m}^2 (\text{g Pt})^{-1}$)	Exchange current density (mA cm^{-2})
(0, 0.5)	284.16	428.64	133.04	43.9	1.48
(0.1, 0.4)	281.24	362.84	118.04	56.4	2.20
(0.2, 0.3)	281.80	395.04	126.48	50.5	1.87
(0.3, 0.2)	286.84	463.16	139.72	33.5	1.24
(0.4, 0.1)	281.00	478.96	145.52	29.4	1.15
(0.5, 0)	289.12	531.68	162.20	12.4	0.93

ORR and reduces the limitation in mass transport within catalyst layer. Further increases of Pt-NW in the composite catalyst, however, result in increases in both charge transfer and gas transfer resistances.

The results of CV scan are shown in Fig. 4 and the corresponding results of ESA analyses are given in Table 1. It is obvious that the composition of electrocatalysts may affect the ESA and catalyst utilization rate in the catalyst layer. The work of Kim et al. [10] has mentioned that the continuously-connected 1D nanostructure of high conductivity of Pt-NWs appears to improve the electrode performance via reducing embedded sites of electrocatalysts and providing smooth pathways for charge transfer. However, the structure of Pt-NWs still suffers from much smaller specific surface area than the conventional Pt/C electrocatalysts especially at conditions of low Pt loadings. Accordingly, a combination of both Pt-NWs and Pt/C may reinforce the advantages but lessen the disadvantages of both electrocatalysts in different nanostructures. The present results show that the case of (Pt-NWs, Pt/C) = (0.1, 0.4) mg cm^{-2} exhibits the highest ESA which reveals that an appropriate mixing ratio of both Pt-NWs and Pt/C in the catalyst layer is very important in order to obtain higher catalyst utilization rate and fuel cell performance, and indeed comes to the reinforcement of the advantages of both electrocatalysts.

In order to investigate the electrochemical kinetics of the electrocatalysts tested, the corresponding Tafel plots are illustrated in

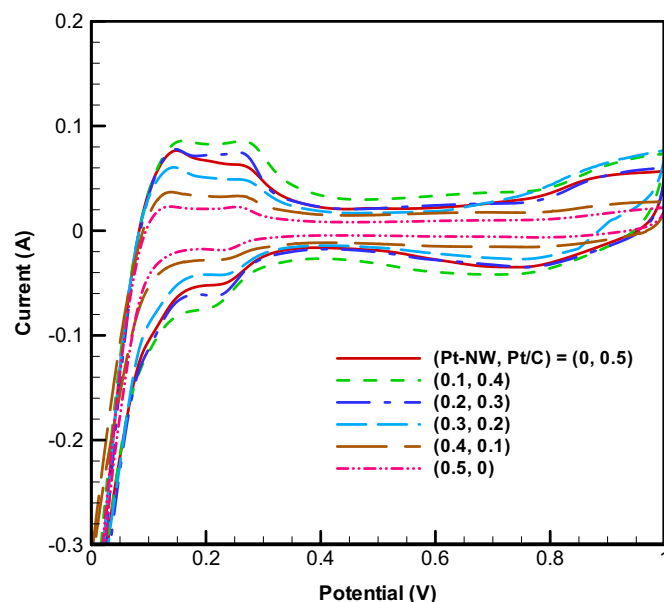


Fig. 4. Cyclic voltammograms of electrodes fabricated with different mixing ratios of Pt-NW and Pt/C in unit of mg cm^{-2} .

Fig. 5 which are plotted based on the results of polarization curves in Fig. 2. The linear Tafel equation is applied to each curve at high overvoltages to calculate the exchange current density from the slope and intercept of a linear fit on the horizontal axis. A higher exchange current density indicates better reaction kinetics which is an important factor for the determination of electrode performance. The results are listed in Table 1 in which the case of (Pt-NWs, Pt/C) = (0.1, 0.4) mg cm^{-2} still gives the highest exchange current density among all the tested cases. The case of pure Pt-NWs shows the lowest exchange current density which indicates lower ORR activity than the case of pure Pt/C. The results also demonstrate that the composite electrocatalysts of Pt-NWs and Pt/C may increase the number of possible reaction sites in the catalyst layer to improve kinetic performance by increasing exchange current density.

3.2. Evaluation of optimal Nafion content

The content of Nafion ionomer in the catalyst layer is also an important factor which may affect the cell performance profoundly. It may influence the gas permeability, catalytic activity, and ionic resistance in the electrode [13]. If the Nafion content is insufficient, it becomes difficult to establish sufficient three-phase boundaries of the reactant gas, electrolyte, and catalyst for electrochemical reaction to take place. Conversely, over loading of Nafion ionomer in the catalyst layer may cause high mass transport resistance and thus lower the cell performance. Accordingly, there exists an optimal Nafion content in the catalyst layer which is an important factor for obtaining good electrode performance.

The polarization curves at different Nafion contents in the cathode catalyst layer are shown in Fig. 6 in which the Pt loadings are all fixed at 0.5 mg cm^{-2} composed of Pt-NWs 0.1 mg cm^{-2} and Pt/C 0.4 mg cm^{-2} . The Nafion content of 20% is obviously insufficient which causes lower three-phase boundaries and the worst performance in all the tested cases. As the Nafion content increases to 25%, the cell performance is improved significantly and the peak power density rises dramatically from 165 to 291 mW cm^{-2} . The case of Nafion content 30% enhances the cell performance further. However, once the Nafion content exceeds 30%, the cell

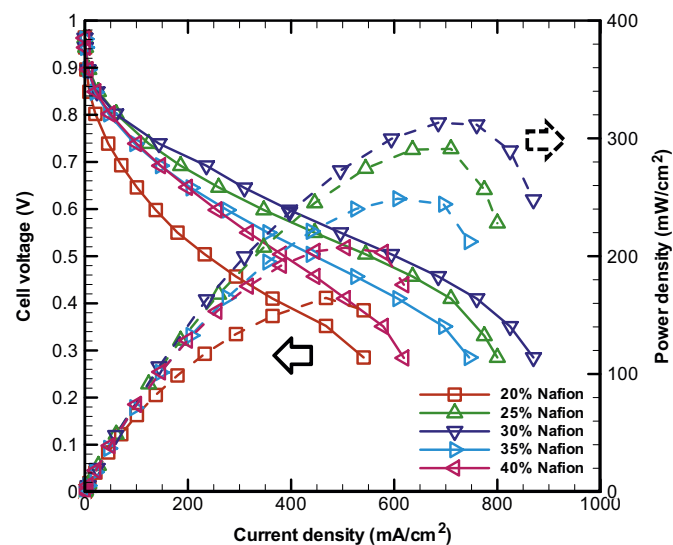


Fig. 6. Polarization and corresponding power density curves at different Nafion ionomer contents in the catalyst layer.

performance begins to descend as shown in the cases of 35% and 40%. Accordingly, we may conclude that the optimal Nafion content for such a composite electrocatalyst in the electrode is about 30%. Note that the optimal Nafion content for the case of bare Pt/C has been investigated in Refs. [12,13]. The work by Antolini et al. [12] found that the optimal Nafion content was about 40 wt% with Pt loading 0.2 mg cm^{-2} in the catalyst layer. In the work by Sasikumar et al. [13], the optimal Nafion content was found to be 20, 40 and 50 wt% at different Pt loadings of 0.5, 0.25, and 0.1 mg cm^{-2} , respectively. Both studies used the same commercial Pt/C catalysts with 20 wt% Pt on Vulcan-XC72 carbon black (E-Tek). Comparing with the present results, it is obvious that the optimal Nafion content depends on the structure and loading of Pt within catalyst layer.

The corresponding EIS spectra measured at current density 500 mA cm^{-2} are demonstrated in Fig. 7 and the simulation results of ohmic resistance, charge transfer resistance, and gas transfer resistance are listed in Table 2. One can see that the influence of Nafion content on ohmic resistance is relatively limited in comparison with the variations of charge transfer resistance and gas transfer resistance. The case of 30 wt% exhibits the lowest ohmic resistance which indicates an appropriate Nafion content in the catalyst layer is helpful for the improvement of proton conductivity and thus produces lower ohmic resistance. The effects on charge transfer resistance and gas transfer resistance are quite significant

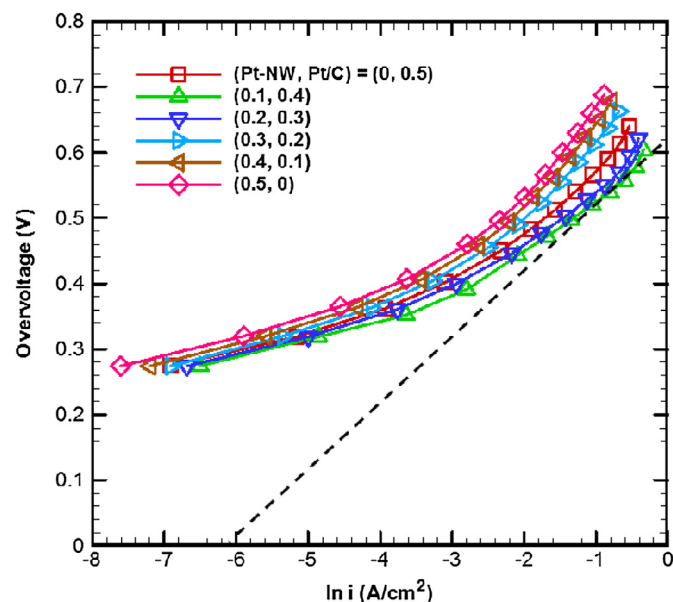


Fig. 5. Tafel plots for the electrodes fabricated with different mixing ratios of Pt-NW and Pt/C in unit of mg cm^{-2} .

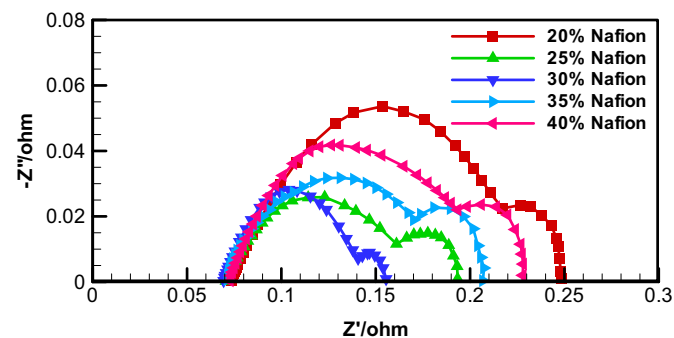


Fig. 7. Impedance spectra measured at current density 500 mA cm^{-2} for different Nafion ionomer contents in the catalyst layer.

Table 2

Characteristics of the MEAs with cathode catalyst layer prepared by different Nafion ionomer contents. The composite electrocatalysts contains 0.1 mg cm^{-2} Pt-NW and 0.4 mg cm^{-2} Pt/C.

Nafion contents (wt%)	Ohmic resistance ($\text{m}\Omega \text{ cm}^2$)	Charge transfer resistance ($\text{m}\Omega \text{ cm}^2$)	Gas transfer resistance ($\text{m}\Omega \text{ cm}^2$)	ESA ($\text{m}^2 (\text{g Pt})^{-1}$)	Exchange current density (mA cm^{-2})
20	293.04	575.68	159.32	33.2	0.85
25	281.24	362.84	118.04	56.4	2.20
30	277.40	287.40	84.52	67.9	4.09
35	284.80	396.08	126.68	44.3	1.54
40	289.36	484.24	137.40	37.1	1.03

as shown in Fig. 7 and Table 2. Both the diameters of high and low frequency arcs first decrease with increasing Nafion content till 30 wt%, and then increase with higher Nafion content. The case of 30 wt% gives the lowest charge transfer resistance and gas transfer resistance, which indicates that the driving force for ORR reaches a maximum value and the mass transport resistance reduces to a minimum simultaneously at Nafion content of 30 wt% approximately. The spectra of CV scan at different Nafion contents are shown in Fig. 8 and the corresponding results of ESA analyses are listed in Table 2. It is found that the content of Nafion ionomer indeed may influence the ESA and catalyst utilization rate in the catalyst layer composed of composite electrocatalysts of Pt-NWs and Pt/C. An insufficient Nafion content, for example, as the case of 20 wt%, exhibits lower ESA value and catalyst utilization rate. On the contrary, an over loading of Nafion ionomer as the typical case of 40 wt% displays lower ESA value due to the increase of reactant transport resistance. For such a composite structure of Pt-NWs and Pt/C, the case of 30 wt% of Nafion content is found to give the highest ESA which also manifests that an appropriate concentration of Nafion ionomer is a crucial factor to improve catalyst utilization rate and fuel cell performance.

Fig. 9 shows the Tafel plots at different Nafion contents based on the results of Fig. 6, which illustrates the variation of electrochemical kinetics of the catalyst layer with Nafion content. Similarly, the linear Tafel equation is applied to each curve at high overvoltages to determine the exchange current density. The results are listed in Table 2 in which the case of 30 wt% apparently

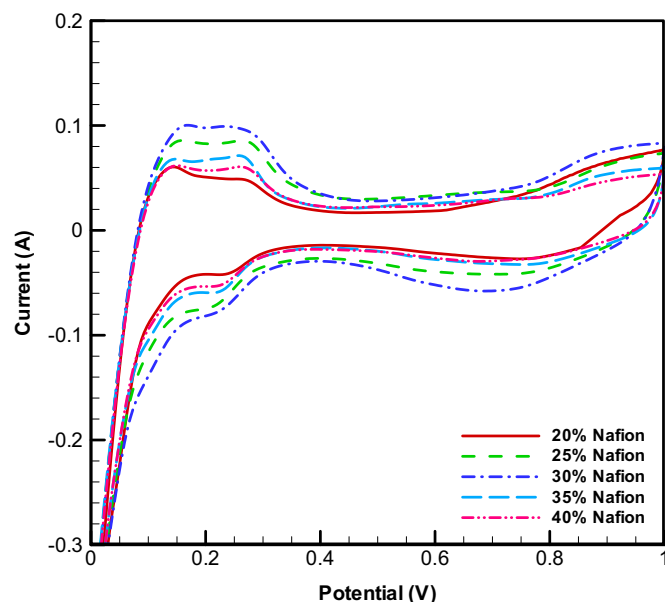


Fig. 8. Cyclic voltammograms of electrodes fabricated with different Nafion ionomer contents in the catalyst layer.

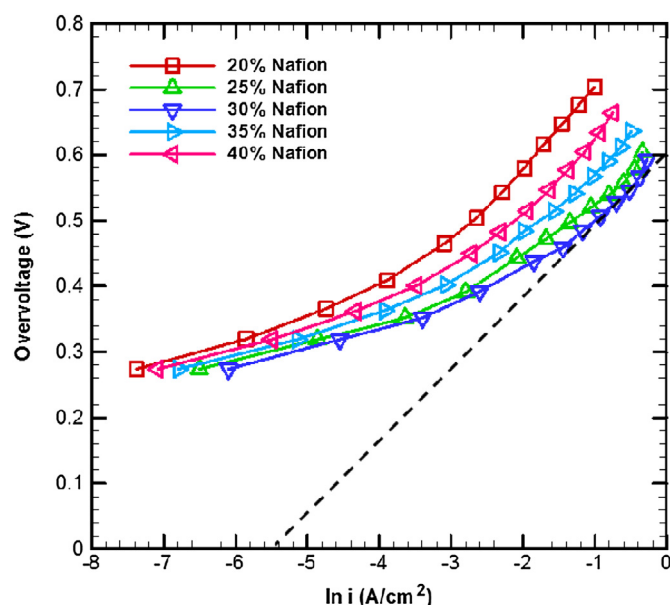


Fig. 9. Tafel plots for the electrodes fabricated with different Nafion ionomer contents in the catalyst layer.

gives the highest exchange current density than the other cases as expected. The case of 20 wt% presents the lowest exchange current density due to insufficient Nafion loading causing lower ORR activity. Oppositely, the case of 40 wt% also presents lower ORR activity because an over Nafion loading may hinder the gas transport efficiency and thus reduce the possible reaction sites and kinetic performance in the composite electrocatalyst layer.

4. Conclusions

In this work, the effect of cathode electrocatalysts composed of electrospun Pt-NWs and commercial Pt/C on PEMFC performance has been investigated in detail. The cathode catalyst layer was fabricated with different mixing ratios of Pt-NWs and Pt/C to explore their ORR activities and influence on cell performance. The results show that an appropriate mixing ratio of Pt-NW and Pt/C in the catalyst layer indeed may present higher performance than the conventional case of pure Pt/C structure. At Pt loading of 0.5 mg cm^{-2} , the case of 0.1 mg cm^{-2} Pt-NWs and 0.4 mg cm^{-2} Pt/C exhibits the optimal cell performance which indicates a small amount of Pt-NWs is favorable to obtain better catalytic structure and performance. Such a composite electrocatalyst is found to give the highest peak power density, ESA, and exchange current density; and lowest cell impedance in all the cases tested. The optimal Nafion content also has been evaluated for the catalyst layer made by composite of Pt-NWs and Pt/C with the specified mixing ratio. The results show that the optimal Nafion content is 30 wt% because the peak power density, ESA and exchange current density are found to be the highest and the cell impedance is the lowest at this optimal concentration of Nafion ionomer. The present study reveals that the application of electrospun Pt-NWs is a potentially possible way to enhance electrode performance. Further studies focus on the morphology, structure, and durability of ORR activity of Pt-NWs would be helpful for the improvement of PEMFC performance. Especially, how the Nafion ionomer disperses on the electrode surface and whether it is preferentially associated with Pt/C or Pt-NWs would be an interesting problem for further exploration. The optimal Nafion loading for the case of pure Pt-NWs is also worth studying, which could provide further understanding for the

relationship between the loading of Pt-NWs and the optimal Nafion content in the catalyst layer.

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